Magnetic resonance in quantum gases

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We use macroscopic equations to find the frequency spectrum of magnetic resonance in a binary paramagnet in an external field. The exchange interaction between the components leads to a shift in the resonance frequencies as compared to their values in the pure components or it leads to the appearance of an extra resonance frequency in the case when the gyromagnetic ratios are the same for the two components. We obtain in the pair interaction approximation for binary quantum gases exact microscopic relations which connect the values of the resonance frequencies with the amplitude of the two-particle scattering. For the kinematic part of the kinetic equation we give a virial expansion which takes into account quantal collective corrections for the interaction of the gas molecules. We construct a solution of the resonance problem through the kinetic-equation method. We discuss in which class of objects the predicted effects can be observed experimentally.

1. INTRODUCTION

The interest in the study of a great variety of properties of quantum gases has recently grown considerably. By quantum gases we usually mean low-density systems in which quantum-mechanical effects in the statistics or in the interaction between particles leads to appreciable quantitative or even qualitatively new effects. To the extent that most real gases condense before quantum effects start to play a considerable role, the traditional objects in this class have always been various isotopes of helium and hydrogen. At the present time large theoretical and experimental efforts have been concentrated on the study of gaseous spin-polarized $^3\mathrm{He}\uparrow$[1,2] and atomic hydrogen $\mathrm{H}\uparrow$.[3,4] However, we shall show in what follows that some quantum effects are inherent not only in the systems just mentioned but have, in principle, macroscopic manifestations also in a mixture of any paramagnetic gases, although the magnitude of the effect, as also shown by the quantum mechanical corrections, decreases as a power law with increasing temperature. We note also that the class of objects which may be considered to be quantum gases and where one may expect an appreciable magnitude of the predicted effects turns out to be rather large. For instance, in a weakly ionized gas or a gas in which there are highly excited atoms, quantum virial corrections caused by the scattering of slow electrons by neutral molecules appreciably affect the thermodynamics of the system right up to a loss of stability, and lead to the existence of long-range correlations of a Fermi liquid type even in the Boltzmann temperature range.[5,6] Methods applied for the study of quantum gases turn out to be very useful also for describing a number of condensed systems such as semi-magnetic semiconductors,[6] superfluid ^{3}He-^{4}He solutions,[7] and others. In what follows we obtain relations valid for any quantum gas with a short range of interaction between the particles. In the concluding part of the paper we consider concrete examples which are of experimental interest.

It is well known that the magnetic resonance frequency of a Fermi liquid in an external magnetic field is independent of the quantities which characterize the interaction between the particles in the liquid and is, as in the case of a perfect gas, determined solely by the gyromagnetic ratio.[8] One shows easily that this conclusion is valid also for an interacting Boltzmann gas. However, the situation is completely changed in the case of two-component (many-component) systems which consist of different particles or of molecules of the same substance but in different internal states. We shall show below that in that case the values of the resonance frequencies depend significantly both on the interaction between particles of different components and on the partial pressures of the two components of the system. If, however, the gyromagnetic ratios for the molecules of the two components are the same the exchange interaction of the subsystems leads to the appearance of a new resonance frequency which corresponds to an additional degree of freedom in a two-component magnetic material all particles of which have the same magnetic moment. The spectrum of the magnetic resonance frequencies can be expressed by means of phenomenological equations in terms of the static susceptibilities of the components and the cross-term "magnetic" virial coefficient. Using the thermodynamic virial expansion in the spirit of Beth and Uhlenbeck's theory[9,10] one can obtain exact relations which connect the value of the resonance frequencies with the amplitude of the two-particle scattering for the case of pair interactions.

The virial expansion of the kinematic part (not the collision integral) of the kinetic equation in a gas is also of fundamental interest. Indeed, to describe the properties of gases in the classical temperature range one uses normally the traditional Boltzmann equation with a left-hand (kinematic) side corresponding to the free motion of the gas particles and all changes in the states of the particles are described by the right-hand side (the collision integral) of the kinetic equation. However, taking into account the interaction of the molecules of the gas requires not only the collision integral but also additional specific terms which can be interpreted as virial corrections to the kinematic part of the Boltzmann equation describing the deviation of the particle distribution function from the Maxwell distribution in a perfect gas, caused by interactions. The necessity to take such correc-

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tions into account is clear already from the following qualitative considerations. Let us assume that we have used the virial expansion for the pressure and, differentiating it, found sound-velocity corrections caused by particle interactions in the gas. We now wish to determine the same correction from the kinetic equation. Integrating this equation over momenta we get the equation of continuity. The flux equation is, as usually, obtained by multiplying the kinetic equation by the momentum and then integrating it over phase space. The above-mentioned integrals of the right-hand side of the Boltzmann equation, i.e., of the collision integral in its normal definition, vanish. It is therefore necessary in order to determine the required corrections to the sound velocity, to take into account in the kinetic equation those virial corrections which contribute to the macroscopic relations which express the conservation laws for the number of particles and for the total momentum, and which we arbitrarily will relate to the kinematic part of the Boltzmann equation. The introduction of such corrections and the possibility produced by them of the propagation in a paramagnetic gas of high-frequency spin waves at sufficiently low temperatures when the de Broglie wavelength of the particles appreciably exceeds the range of the interaction has been considered before.[5,6]

In the present paper we propose for the kinematic part of the kinetic equation a virial expansion which is valid for any temperatures. Based on the equations obtained, we evaluate the spectrum of the spatially uniform magnetization oscillations in a two-component paramagnetic gas in an external field. The spectra of the paramagnetic resonance frequencies found by the kinetic-equation method and those found by means of the macroscopic equations and thermodynamic relations are the same.

2. MACROSCOPIC EQUATIONS

To begin with we shall consider the case of not too strong magnetic fields, $\hbar\gamma_{1,2}H \ll T$, where $\gamma_{1,2}$ are the gyromagnetic ratios of the particles of the first and the second components, $\mathbf{H}$ is the field strength (because the static magnetic permeability is small we shall not distinguish between $\mathbf{H}$ and $\mathbf{B}$), and T the temperature. Such a situation is in practice most often realized. In that case the magnetic moments per unit volume for the two components $\mathbf{M}_1$ and $\mathbf{M}_2$ are also small. In the exchange approximation the free energy density F of a uniformly magnetized two-component magnetic substance is then given by the well known phenomenological expansion:

$$F=\frac{M_1^2}{2\chi_{11}}+\frac{M_2^2}{2\chi_{22}}+\frac{\mathbf{M}_1\mathbf{M}_2}{\chi_{12}}-(\mathbf{M}_1+\mathbf{M}_2)\mathbf{H}-\frac{H^2}{8\pi}. \tag{2.1}$$

The off-diagonal elements $\chi_{12}=\chi_{21}$ of the symmetric static susceptibility matrix $\|\chi_{ik}\|$, $i,k=1,2$ describe the exchange interaction between the components of the system. Neglecting dissipation, the macroscopic dynamics of the magnetization is determined by the classical Landau-Lifshitz equations:

$$\frac{\partial\mathbf{M}_1}{\partial t}=\gamma_1[\mathbf{H}_1\times\mathbf{M}_1],\quad \frac{\partial\mathbf{M}_2}{\partial t}=\gamma_2[\mathbf{H}_2\times\mathbf{M}_2], \tag{2.2}$$

where the effective fields $\mathbf{H}_1$ and $\mathbf{H}_2$ are found by varying the free energy (2.1):

$$\begin{aligned}\mathbf{H}_1&=-\left(\frac{\delta F}{\delta\mathbf{M}_1}\right)_{\mathbf{H},\mathbf{M}_2}=-\frac{\mathbf{M}_1}{\chi_{11}}+\mathbf{H}-\frac{\mathbf{M}_2}{\chi_{12}},\\ \mathbf{H}_2&=-\left(\frac{\delta F}{\delta\mathbf{M}_2}\right)_{\mathbf{H},\mathbf{M}_1}=-\frac{\mathbf{M}_2}{\chi_{22}}+\mathbf{H}-\frac{\mathbf{M}_1}{\chi_{12}}.\end{aligned} \tag{2.3}$$

The magnetization distribution will be looked for in the form of small deviations of the vectors $\mathbf{M}_1$ and $\mathbf{M}_2$ from its equilibrium direction along $\mathbf{H}$:

$$\mathbf{M}_i(t)=\mathbf{M}_{i0}+M_{i0}\mathbf{m}_i(t),\quad i=1,\ 2,\quad \mathbf{m}_i\perp\mathbf{M}_{i0},\quad \mathbf{m}_i\infty e^{-i\omega t}, \tag{2.4}$$

where $\mathbf{M}_{i0}$ are the equilibrium values of the vectors $\mathbf{M}_1$ and $\mathbf{M}_2$ produced by the external magnetic field:

$$\begin{aligned}&\mathbf{M}_{10}=(\chi_{22}^{-1}-\chi_{12}^{-1})\mathbf{H}/\Delta,\quad \mathbf{M}_{20}=(\chi_{11}^{-1}-\chi_{12}^{-1})\mathbf{H}/\Delta,\\ &\Delta=(\chi_{11}\chi_{22})^{-1}-\chi_{12}^{-2}.\end{aligned} \tag{2.5}$$

Substituting (2.3) to (2.5) into the dynamic equations (2.2) we find

$$\begin{aligned}-i\omega m_{1x}&=(\Omega_1-\omega_{H1})m_{1y}-\Omega_1 m_{2y},\\ -i\omega m_{1y}&=(\omega_{H1}-\Omega_1)m_{1x}+\Omega_1 m_{2x},\\ -i\omega m_{2x}&=(\Omega_2-\omega_{H2})m_{2y}-\Omega_2 m_{1y},\\ -i\omega m_{2y}&=(\omega_{H2}-\Omega_2)m_{2x}+\Omega_2 m_{1x}.\end{aligned} \tag{2.6}$$

We used here the following notation:

$$\Omega_1=\gamma_1 M_{20}/\chi_{12},\quad \Omega_2=\gamma_2 M_{10}/\chi_{12},\quad \omega_{Hi}=\gamma_i H,\quad i=1,\ 2. \tag{2.7}$$

Introduction of the circular components $m_k^{(-)}=m_{kx}-im_{ky}$ still further simplifies Eqs. (2.6):

$$\begin{aligned}&(\omega_{H1}-\Omega_1-\omega)m_1^{(-)}+\Omega_1 m_2^{(-)}=0,\\ &\Omega_2 m_1^{(-)}+(\omega_{H2}-\Omega_2-\omega)m_2^{(-)}=0.\end{aligned} \tag{2.8}$$

The compatibility condition for the system (2.8) leads to an obvious quadratic dispersion equation, the roots of which determine the spectrum of the uniform magnetic resonance frequencies:

$$\omega_{1,2}=\frac{(\omega_{H1}-\Omega_1)+(\omega_{H2}-\Omega_2)}{2}\mp\left\{\frac{[(\omega_{H1}-\Omega_1)-(\omega_{H2}-\Omega_2)]^2}{4}+\Omega_1\Omega_2\right\}^{1/2}. \tag{2.9}$$

If $\gamma_1=\gamma_2\equiv\gamma$ the expressions for the resonance frequencies take on an extremely simple form:

$$\omega_1=\gamma H,\quad \omega_2=\gamma H-(\Omega_1+\Omega_2)=\gamma[H-(M_{10}+M_{20})/\chi_{12}]. \tag{2.10}$$

We see from Eqs. (2.8) that in the first type of oscillations $\mathbf{m}_1=\mathbf{m}_2$ i.e., this solution is the normal precession of the total magnetic moment of the system $\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2$, $M=M_{10}+M_{20}$ around the applied magnetic field with Larmor frequency γH. On the other hand, in the second type of oscillations $\mathbf{m}_1=-(\Omega_1/\Omega_2)\mathbf{m}_2=-(M_{20}/M_{10})\mathbf{m}_2$, i.e., the total magnetization $\mathbf{M}$ is conserved and does not oscillate, although the magnetic moments of each of its components $\mathbf{M}_1$ and $\mathbf{M}_2$ perform periodic motions with frequency ω_2 as follows from (2.10). The relative motion of the vectors $\mathbf{M}_1$ and $\mathbf{M}_2$ proceeds in such a way that $\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2=\mathbf{M}_{10}+\mathbf{M}_{20}=\text{const}$.

If $\gamma_1 \neq \gamma_2$ and the corrections due to the exchange interaction between the components is not too large, i.e., $|\Omega_1 - \Omega_2| \ll |\omega_{H1} - \omega_{H2}|$, we can also write down simple formulae for the resonance frequencies

$$\omega_1=\omega_{H1}-\Omega_2=\gamma_1(H-M_{20}/\chi_{12}),$$
$$\omega_2=\omega_{H2}-\Omega_1=\gamma_2(H-M_{10}/\chi_{12}), \qquad (2.11)$$

which determine the difference of the precession frequencies of the vectors $\mathbf{M}_1$ and $\mathbf{M}_2$ in a constant magnetic field from the corresponding Larmor frequencies $\gamma_1 H$ and $\gamma_2 H$.

We shall in what follows be interested in resonance effects in paramagnetic dilute mixtures such that all virial corrections describing the interaction of the particles will contain additional powers in the small density as compared to the analogous terms in a perfect gas. Taking only the pair interaction into account we can therefore use in the second virial coefficient approximation the values of M_{10} and M_{20} neglecting interactions, i.e., those in a perfect gas, rather than the exact expressions (2.5). For the frequency spectrum we finally have

$$\omega_1=\gamma_1 H(1-\chi_{22}^{(0)}/\chi_{12}), \quad \omega_2=\gamma_2 H(1-\chi_{11}^{(0)}/\chi_{12}), \qquad (2.12)$$

if $\gamma_1 \neq \gamma_2$ or

$$\omega_1=\gamma H, \quad \omega_2=\gamma H[1-(\chi_{11}^{(0)}+\chi_{22}^{(0)})/\chi_{12}], \qquad (2.13)$$

when $\gamma_1 = \gamma_2 \equiv \gamma$. Here $\chi_{11}^{(0)}$ and $\chi_{22}^{(0)}$ are the static paramagnetic susceptibilities of the two components in the perfect gas approximation.

3. THERMODYNAMIC VIRIAL EXPANSION

We now try to perform a microscopic calculation of those phenomenological characteristics on which the shift in the magnetic resonance frequencies (2.12), (2.13) depend. The value of the susceptibilities $\chi_{11}^{(0)}$ and $\chi_{22}^{(0)}$ is calculated from the usual Curie-Weiss formula:

$$\chi_{kk}^{(0)}=\frac{\gamma_k^2}{T}\frac{S_k(S_k+1)}{3}N_k, \qquad k=1,2, \qquad (3.1)$$

where N_k and S_k are the number of molecules per unit volume and the spin of a molecule of the k th component. To fix the ideas we shall in what follows consider such gases for which the particles possess only spin (electronic or nuclear) but no orbital angular momentum. To obtain the quantity χ_{12} it is necessary to evaluate the cross-term virial coefficient which describes the exchange interaction between two spin-polarized components. The thermodynamic expansion in powers of the small density (or activity) corresponds to a functional expansion in a series in powers of the distribution function of a perfect gas (single-particle density matrix for spin-polarized gases). In accordance with this, the correction to the free energy (per unit volume) caused by the pair interaction of particles from different components can be written in the form

$$\Delta F_{12}=\mathrm{Sp}_{S_1,S_2}\sum_{\mathbf{p}_1,\mathbf{p}_2}\Phi_{S_1S_2}(\mathbf{p}_1,\mathbf{p}_2)n_{1S_1}^{(0)}(\mathbf{p}_1)n_{2S_2}^{(0)}(\mathbf{p}_2), \qquad (3.2)$$

where $n_{kS_k}^{(0)}(\mathbf{p})$ is the polarization density matrix in the perfect gas of the particles of the k th component. For the sake of simplicity we shall study the region of not too high temperatures when, in the particle collision process, no changes occur in their internal states, so that, for instance, no rotational degrees of freedom of the molecules are excited. In that case the interaction function $\Phi_{S_1S_2}(\mathbf{p}_1,\mathbf{p}_2)$ from (3.2) can be expressed in terms of the amplitude of the elastic two-particle scattering and, taking into account the internal states, reduces simply to introducing the corresponding statistical weights as factors and they drop out of the final results.

In the non-relativistic approximation the potential for the interaction of two particles does not depend explicitly on the spins and is thus not affected by the external magnetic field. The spin dependence of the function $\Phi_{S_1S_2}(\mathbf{p}_1,\mathbf{p}_2)$ is caused solely by exchange effects. Moreover, in the pair interaction approximation used $\Phi_{S_1S_2}(\mathbf{p}_1,\mathbf{p}_2)$ is not a functional of $n_{kS_k}^{(0)}(\mathbf{p})$, i.e., is independent of the magnetic moments of the components and thus of the external magnetic field. The interaction function in (3.2) can thus be evaluated neglecting the external field. As far as the spin matrix $n_{kS_k}^{(0)}$ is concerned, in weak fields it can be expressed in terms of $\mathbf{H}$ using the obvious relations:

$$n_{kS_k}^{(0)}=n_k^{(0)}\left(1+\frac{\gamma_k\mathbf{S}_k\mathbf{H}}{T}\right)=n_k^{(0)}\left[1+\frac{3\mathbf{S}_k\mathbf{M}_k}{\gamma_kN_kS_k(S_k+1)}\right],$$
$$k=1,2, \qquad (3.3)$$

where $n_k^{(0)}$ is the Maxwellian distribution function:

$$n_k^{(0)}(\mathbf{p})=\exp\left(\frac{\mu_k^{(0)}}{T}-\frac{p^2}{2m_kT}\right)$$
$$=\frac{N_k}{2S_k+1}\left(\frac{2\pi\hbar^2}{m_kT}\right)^{3/2}\exp(-p^2/2m_kT). \qquad (3.4)$$

In Eq. (3.4) $\mu_k^{(0)}$ and m_k are the chemical potential and the mass of the particles of the k th component.

We consider the practically important case when the spin of the particles of one of the components is one-half: $S_2 = \frac{1}{2}$. In that case any function of the operator S_2 reduces to a linear one and the interaction function can in the exchange approximation be written in the form

$$\Phi_{S_1S_2}(\mathbf{p}_1,\mathbf{p}_2)=\Psi(\mathbf{p}_1,\mathbf{p}_2)+\xi(\mathbf{p}_1,\mathbf{p}_2)\mathbf{S}_1\mathbf{S}_2. \qquad (3.5)$$

Substituting (3.3) and (3.5) into (3.2) and using the formula

$$\mathrm{Sp}_S(\mathbf{SA})(\mathbf{SB})={}^1/_3S(S+1)(2S+1)\mathbf{AB}, \qquad (3.6)$$

to sum over the spins we get

$$\Delta F_{12}=(2S_1+1)(2S_2+1)\sum_{\mathbf{p}_1,\mathbf{p}_2}\left\{\psi(\mathbf{p}_1,\mathbf{p}_2)+\frac{\mathbf{M}_1\mathbf{M}_2}{\gamma_1\gamma_2N_1N_2}\xi(\mathbf{p}_1,\mathbf{p}_2)\right\}$$
$$\times n_1^{(0)}(\mathbf{p}_1)n_2^{(0)}(\mathbf{p}_2). \qquad (3.7)$$

Comparing (3.7) and (2.1) we find the off-diagonal element of the magnetic susceptibility matrix

$$\chi_{12}^{-1}=\frac{(2S_1+1)(2S_2+1)}{\gamma_1\gamma_2N_1N_2}\sum_{\mathbf{p}_1,\mathbf{p}_2}\xi(\mathbf{p}_1,\mathbf{p}_2)n_1^{(0)}(\mathbf{p}_1)n_2^{(0)}(\mathbf{p}_2). \qquad (3.8)$$

The rest of the problem consists in expressing the function $\xi(\mathbf{p}_1,\mathbf{p}_2)$ in terms of the exact microscopic characteristic—the two-particle scattering amplitude. To do that we apply the

Beth and Uhlenbeck method[9,10] to our two-component system.

The Gibbs distribution for the two-component system is given by the well known expression

$$w_{n,N_1,N_2}=\exp\left\{\frac{\Omega+\mu_1N_1+\mu_2N_2-E_{n,N_1,N_2}}{T}\right\}, \tag{3.9}$$

where the index n numbers the various states. Normalizing the distribution (3.9) to unity we get the thermodynamics potential in the form

$$\Omega=-T\ln\sum_{N_1}e^{\mu_1N_1/T}\sum_{N_2}e^{\mu_2N_2/T}\sum_{n}e^{-E_{n,N_1,N_2}/T}. \tag{3.10}$$

Expanding this expression in powers of the activity $\exp(\mu_k^{(0)}/T)\ll 1$ and restricting ourselves to the pair interaction we find

$$\Omega=\Omega_{11}+\Omega_{22}+\Omega_{12},\quad \Omega_{12}=-T\sum_n\exp\left\{\frac{\mu_1^{(0)}+\mu_2^{(0)}-E_{n,1,1}}{T}\right\}, \tag{3.11}$$

where $\Omega_{11}+\Omega_{22}$ is the thermodynamic potential of the system, neglecting the interaction between the components albeit including the virial corrections connected with the interaction and the identical nature of the particles in each separate component. The energy spectrum of two interacting particles from different components will, as usual be classified by separating the motion of the pair as a whole with total momentum $\mathbf{P}$ and considering the relative motion of the particles in the center of mass sytem with momentum $\mathbf{q}$:

$$\begin{gathered}E_{n,1,1}=P^2/2M+q^2/2m,\quad M=m_1+m_2,\quad m=m_1m_2/M,\\ \mathbf{p}_1=(m_1/M)\mathbf{P}-\mathbf{q},\quad \mathbf{p}_2=(m_2/M)\mathbf{P}+\mathbf{q}.\end{gathered} \tag{3.12}$$

We assume that in $E_{n,1,1}$ of (3.12) there are no discrete energy levels, corresponding to bound states of a pair of molecules.

The total spinof the pair of particles considered can take on two values: $S_1\pm\frac{1}{2}$. The corresponding values of the scattering amplitude and the partial scattering phases will be denoted by f_+, f_-; $\delta_l^{(+)}$, $\delta_l^{(-)}$. We assume that the spins of absolutely all particles of the system, including both components, are polarized in the same way. Substituting (3.12) into (3.11) and proceeding similarly as in Refs. 9, 10 in evaluating the partition function we get

$$\Omega_{12}^{(+)}=-T\sum_{\mathbf{P}}\exp\left\{\frac{\mu_1^{(0)}+\mu_2^{(0)}}{T}-\frac{P^2}{2MT}\right\}\times\frac{1}{\pi}\sum_l\int_0^\infty(2l+1)\frac{d\delta_l^{(+)}}{dq}e^{-q^2/2mT}\,dq, \tag{3.13}$$

or, expressing $\delta_l^{(+)}$ in terms of f_+ we have

$$\Omega_{12}^{(+)}=\sum_{\mathbf{P},\mathbf{q}}\exp\left\{\frac{\mu_1^{(0)}+\mu_2^{(0)}}{T}-\frac{P^2}{2MT}-\frac{q^2}{2mT}\right\}A_+(\mathbf{q}), \tag{3.14}$$

$$A_\pm(\mathbf{q})=-\frac{2\pi\hbar^2}{m}\left\{\operatorname{Re}f_\pm(0,q)+\frac{2mT}{\hbar}\left[\operatorname{Re}f_\pm(\theta,q)\frac{\partial}{\partial q}\operatorname{Im}f_\pm(\theta,q)-\operatorname{Im}f_\pm(\theta,q)\frac{\partial}{\partial q}\operatorname{Re}f_\pm(\theta,q)\right]\right\}. \tag{3.15}$$

According to the theorem about small corrections, $\Omega_{12}=\Delta F_{12}$. Therefore, evaluating ΔF_{12} using Eq. (3.2) in which we must take it into account that the spin polarization of the particles is the same, substituting the distribution function (3.4) and changing to the variables $\mathbf{P}$ and $\mathbf{q}$ in accord with (3.12), and then comparing the result with (3.14) and (3.15), we find the connection between the functions ψ, ξ, and f_+:

$$\psi\left(\frac{m_1}{M}\mathbf{P}-\mathbf{q},\frac{m_2}{M}\mathbf{P}+\mathbf{q}\right)+\frac{S_1}{2}\xi\left(\frac{m_1}{M}\mathbf{P}-\mathbf{q},\frac{m_2}{M}\mathbf{P}+\mathbf{q}\right)=A_+(\mathbf{q}). \tag{3.16}$$

Perfectly similar calculations for two completely polarized components whose spin polarization vectors are, however, antiparallel give one more relation between the above functions:

$$\psi\left(\frac{m_1}{M}\mathbf{P}-\mathbf{q},\frac{m_2}{M}\mathbf{P}+\mathbf{q}\right)-\frac{S_1+1}{2}\xi\left(\frac{m_1}{M}\mathbf{P}-\mathbf{q},\frac{m_2}{M}\mathbf{P}+\mathbf{q}\right)=A_-(\mathbf{q}). \tag{3.17}$$

From (3.16), (3.17) we get at once

$$\psi=\frac{S_1+1}{2S_1+1}A_++\frac{S_1}{2S_1+1}A_-,\quad \xi=\frac{2}{2S_1+1}(A_+-A_-), \tag{3.18}$$

which determines the required connection between the interaction function Φ and the scattering amplitude.

It is clear from (3.15) to (3.18) that as the function ξ depends only on the momentum of the relative motion $\xi(\mathbf{p}_1,\mathbf{p}_2)\equiv\xi(\mathbf{q})$ we can in Eq. (3.8) for χ_{12}^{-1} easily integrate over the center-of-mass momentum variables:

$$\chi_{12}^{-1}=\frac{1}{\gamma_1\gamma_2}\frac{1}{(2\pi mT)^{3/2}}\int\xi(\mathbf{q})e^{-q^2/2mT}\,d^3q\equiv\frac{X(T)}{\gamma_1\gamma_2}. \tag{3.19}$$

Thus, Eqs. (2.12), (2.13), (3.1), and (3.19) determine ultimately the shift of the magnetic resonance frequency in an interacting two-component gas. When $S_1\neq\frac{1}{2}$

$$\begin{gathered}\omega_1=\gamma_1H\left[1-\frac{\gamma_2}{4\gamma_1}\frac{X(T)}{T}N_2\right],\\ \omega_2=\gamma_2H\left[1-\frac{S_1(S_1+1)}{3}\frac{\gamma_1}{\gamma_2}\frac{X(T)}{T}N_1\right].\end{gathered} \tag{3.20}$$

When $S_1=\frac{1}{2}$, $\gamma_1=\gamma_2\equiv\gamma$

$$\omega_1=\gamma H,\quad \omega_2=\gamma H\left[1-\frac{X(T)}{4T}N\right],\quad N=N_1+N_2. \tag{3.21}$$

At low temperatures $T\ll\hbar^2/mr_0^2$ (r_0 is the range of the interaction) we have in the limit of slow collisions

$$f_\pm(\theta,q)=-a_\pm(1-iqa_\pm/\hbar),\quad q|a_\pm|/\hbar\ll 1,\quad |a_\pm|\sim r_0. \tag{3.22}$$

The quantity $X(T)$ then depends very weakly on the temperature

$$X(T)=\frac{2}{2S_1+1}\frac{2\pi\hbar^2}{m}(a_+-a_-)\left[1+\frac{2mT}{\hbar^2}(a_+^2+a_-^2+a_+a_-)\right], \tag{3.23}$$

and the shift of the resonance frequencies turns out in the main approximation to be inversely proportional to T:

$$\frac{\chi_{kk}^{(0)}}{\chi_{12}}=\frac{2\pi}{3}S_k(S_k+1)\frac{\gamma_k^2}{\gamma_1\gamma_2}\left(\frac{\Lambda_T}{a_2}\right)^2(N_ka_2^3), \tag{3.24}$$

where we have introduced the thermal de Broglie wavelength Λ_T and the exchange scattering length a_2:

$$\Lambda_T=\hbar/mv_T=\hbar/(mT)^{1/2}, \qquad a_2=2(a_+-a_-)/(2S_1+1). \tag{3.25}$$

As in a Boltzmann gas we have always $\Lambda_T \ll N_k^{-1/3}$ and $N_k^{1/3}|a_2| \ll 1$, the frequency shift (3.24) turns out to be small to the extent that the virial corrections are small.

We note that in Eqs. (3.21) and (3.24) for the frequency shift there are for the case $\gamma_1=\gamma_2\equiv\gamma$ no parameters characterizing the difference of the particles of the different components from one another such that when they tend to zero the effect also vanishes. Nonetheless when the two components are identical (a one-component gas) the above mentioned expressions are inapplicable and there is no effect. The fact is that there is no group of parameters for which there exists a continuous transition between different and identical particles. Particles are either always identical or different (even for arbitrarily small changes in the parameters) and this property can change only abruptly. In this sense the situation is similar to the well known Gibbs paradox about the entropy of a mixture of two ideal gases.

4. VIRIAL EXPANSION OF THE DISTRIBUTION FUNCTION

When using the kinetic equation we need in what follows the virial corrections to the single-particle polarization density matrix of a perfect gas. The entropy of an interacting gas can be expressed in terms of the occupation number of various quantum states through an essentially purely combinatorial relation

$$\tilde{S}_k=\mathrm{Sp}_{s_k}\sum_{\mathbf{p}}\{-n_{ks_k}(\mathbf{p})\ln n_{ks_k}(\mathbf{p}) \mp[1\mp n_{ks_k}(\mathbf{p})]\ln[1\mp n_{ks_k}(\mathbf{p})]\}, \quad k=1,2. \tag{4.1}$$

The upper and lower signs in (4.1) refer to systems of fermions and bosons, respectively. The total energy E of the system is a functional of the occupation numbers for both components: $E=E\{n_{1S_1}, n_{2S_2}\}$. The quantities n_{kS_k} themselves are normalized to the total number of particles (per unit volume):

$$\mathrm{Sp}_{s_k}\sum_{\mathbf{p}} n_{ks_k}(\mathbf{p})=N_k. \tag{4.2}$$

Maximizing the total entropy $\tilde{S}_1+\tilde{S}_2$ with the additional conditions that the total energy E and the numbers of particles for each component N_1 and N_2 are constant we find the equilibrium particle momentum distribution functions:

$$n_{ks_k}=[\exp(\lambda_E\varepsilon_{ks_k}+\lambda_{N_k})\pm 1]^{-1} \approx \exp(-\lambda_E\varepsilon_{ks_k}-\lambda_{N_k}), \quad k=1,2, \tag{4.3}$$

where λ_E, λ_{N_1}, λ_{N_2} are the respective Langrangian multipliers in the conditional extremum problem and the peculiar excitation energy ε_{kS_k} is determined by the first functional derivative of the energy:

$$\varepsilon_{ks_k}=\delta E/\delta n_{ks_k}. \tag{4.4}$$

The meaning of the undetermined Langrangian multipliers is, as usual, determined by using the thermodynamic identity for a given volume:

$$dE=Td\tilde{S}+\mu_1 dN_1+\mu_2 dN_2, \tag{4.5}$$

so that $\lambda_E=T^{-1}$, $\lambda_{N_k}=-\mu_k/T$.

The contribution of the particle pair interaction to the total energy of the system can in the general case be written in the form of the following virial expansion:

$$E_{int}=\sum_{k,\ m=1}^{2}\mathrm{Sp}_{S_kS'_m}\sum_{\mathbf{p}_1,\mathbf{p}_2}\Gamma^{(km)}_{S_kS'_m}(\mathbf{p}_1,\mathbf{p}_2)\,n^{(0)}_{kS_k}(\mathbf{p}_1)\,n^{(0)}_{mS'_m}(\mathbf{p}_2),$$

$$\Gamma^{(km)}_{S_kS'_m}=\Gamma^{(mk)}_{S'_mS_k}. \tag{4.6}$$

Comparing (3.2) and (4.6) and using the theorem about small corrections we find that

$$2\Gamma^{(12)}_{s_1s_2}(\mathbf{p}_1,\mathbf{p}_2)=\Phi_{s_1s_2}(\mathbf{p}_1,\mathbf{p}_2). \tag{4.7}$$

As to the quantities $\Gamma^{(kk)}_{S_kS_{k'}}$, they characterize the interactions of the particles of the k th component with one another and do not enter into the final answer. We shall therefore not give here the exact microscopic expressions for the $\Gamma^{(kk)}_{S_kS_{k'}}$. Within our accuracy (second virial approximation) we may assume that the true occupation numbers occur in the energy (4.6) and not the distribution function of a perfect gas, i.e., $n_{kS_k}(\mathbf{p})\approx n^{(0)}_{kS_k}(\mathbf{p})$. Then varying expression (4.6) in accordance with (4.4) we find the virial correction to the energy per particle caused by the interaction with all other gas molecules:

$$\varepsilon^{(int)}_{ks_k}=2\,\mathrm{Sp}_{s_k'}\sum_{\mathbf{p}_2}\Gamma^{(kk)}_{s_ks_k'}(\mathbf{p},\mathbf{p}_2)\,n^{(0)}_{ks_k'}(\mathbf{p}_2) +\mathrm{Sp}_{s_2}\sum_{\mathbf{p}_2}\Phi_{s_1s_2}(\mathbf{p},\mathbf{p}_2)\,n^{(0)}_{ms_2}(\mathbf{p}_2), \quad m\neq k. \tag{4.8}$$

Substituting (4.8) into (4.3) we find finally the difference between the actual occupation numbers and their values in the perfect gas:

$$\begin{aligned}\delta n^{(int)}_{1s_1}(\mathbf{p})&=\frac{\partial n^{(0)}_{1s_1}}{\partial\varepsilon_{1s_1}}\varepsilon^{(int)}_{1s_1}\\&=-\frac{1}{T}\mathrm{Sp}_{s_2}\sum_{\mathbf{p}_2}\Phi_{s_1s_2}(\mathbf{p},\mathbf{p}_2)\,n^{(0)}_{1s_1}(\mathbf{p})\,n^{(0)}_{2s_2}(\mathbf{p}_2)\\&\quad-\frac{2}{T}\mathrm{Sp}_{1s_1'}\sum_{\mathbf{p}_2}\Gamma^{(11)}_{s_1s_1'}(\mathbf{p},\mathbf{p}_2)\,n^{(0)}_{1s_1}(\mathbf{p})\,n^{(0)}_{1s_1'}(\mathbf{p}_2),\end{aligned} \tag{4.9}$$

$$\begin{aligned}\delta n^{(int)}_{2s_2}(\mathbf{p})&=\frac{\partial n_{2s_2}}{\partial\varepsilon_{2s_2}}\varepsilon^{(int)}_{2s_2}\\&=-\frac{1}{T}\mathrm{Sp}_{s_1}\sum_{\mathbf{p}_2}\Phi_{s_1s_2}(\mathbf{p},\mathbf{p}_2)\,n^{(0)}_{1s_1}(\mathbf{p}_2)\,n^{(0)}_{2s_2}(\mathbf{p})\\&\quad-\frac{2}{T}\mathrm{Sp}_{s_2'}\sum_{\mathbf{p}_2}\Gamma^{(22)}_{s_2s_2'}(\mathbf{p},\mathbf{p}_2)\,n^{(0)}_{2s_2}(\mathbf{p})\,n^{(0)}_{2s_2'}(\mathbf{p}_2).\end{aligned}$$

Similar expressions for a single-component gas of spinless particles were obtained in Ref. 11 by other means, namely, through a direct evaluation of the average value of the operator of the number of particles in a given quantum state.

5. KINETIC EQUATION METHOD

For a consistent derivation of the quantum kinetic equation describing non-equilibrium particle momentum distributions we need an explicit expression for the Hamiltonian of the system, which in the case of a binary gas has the following form:

$$\hat{H}=\sum_{k=1}^{2}\sum_{1,2}T^{(k)}(1,2)\,\hat{a}_{k_1}{}^{+}\hat{a}_{k_2}+\hat{U}_{int},$$

$$\hat{U}_{int}=\frac{1}{2}\sum_{i,k=1}^{2}\sum_{1,2,3,4}U^{(ik)}(1,2;3,4)\,\hat{a}_{i1}\hat{a}_{k2}^{+}\hat{a}_{k3}\hat{a}_{i4},\qquad(5.1)$$

where $T^{(k)}$ is the single-particle energy spectrum for particles of each kind, $U^{(kk)}$ the matrix element of the pair interaction between molecules of the k th component, $U^{(12)}$ characterizes the interaction between particles from different components, and $\hat{a}_{k1}^{+}$ and $\hat{a}_{k1}$ are the creation and annihilation operators for particles of the k th component in the state $|1\rangle$. The commutation relations between the creation and annihilation operators for particles of the same kind are determined by their statistics (fermions or bosons):

$$\hat{a}_{k1}\hat{a}_{k2}{}^{+}\pm\hat{a}_{k2}{}^{+}\hat{a}_{k1}=\delta_{12},\qquad \hat{a}_{k1}{}^{+}\hat{a}_{k2}{}^{+}\pm\hat{a}_{k2}{}^{+}\hat{a}_{k1}{}^{+}=\hat{a}_{k1}\hat{a}_{k2}\pm\hat{a}_{k2}\hat{a}_{k1}=0.\qquad(5.2)$$

The second quantization operators for particles of different kinds, of course, commute with one another:

$$[\hat{a}_{k1}\hat{a}_{i2}{}^{+}]=[\hat{a}_{k1}\hat{a}_{i2}]=[\hat{a}_{k1}{}^{+}\hat{a}_{i2}{}^{+}]=0,\quad i\neq k.\qquad(5.3)$$

The single-particle density matrices for particles of each of the components are given by the usual relations

$$\hat{n}_{ks_k}(1,2)=\langle\hat{a}_{k1}{}^{+}\hat{a}_{k2}\rangle.\qquad(5.4)$$

The kinetic equations for the density matrices $\hat{n}_{kS_k}$ will be obtained in analogy with Ref. 12 by averaging the Liouville equation for the density operators $\hat{a}_{k1}^{+}\hat{a}_{k2}$:

$$i\hbar\frac{\partial}{\partial t}\langle\hat{a}_{k1}{}^{+}\hat{a}_{k2}\rangle=\langle[\hat{a}_{k1}{}^{+}\hat{a}_{k2},\hat{H}]\rangle.\qquad(5.5)$$

Substituting (5.1) and (5.4) into (5.5) and using the commutation relations (5.2), (5.3) we get

$$\frac{\partial\hat{n}_{kS_k}}{\partial t}-\frac{i}{\hbar}[\hat{T}^{(k)},\hat{n}_{kS_k}]=-\frac{i}{\hbar}\hat{Y}_{kS_k},\quad k=1,2,\qquad(5.6)$$

where the matrix $\hat{Y}_{kS_k}$ is given by the following expression:

$$\begin{aligned}\hat{Y}_{ks_k}(1,2)=\sum_{3,4,5}\{&U^{(kk)}(2,5;4,3)\hat{\mathfrak{N}}_k(1,5;4,3)\\&-U^{(kk)}(3,4;5,1)\hat{\mathfrak{N}}_k(3,4;5,2)\\&+\hat{n}_{is_i}(3,4)[U^{(12)}(2,3;4,5)\hat{n}_{ks_k}(1,5)\\&-U^{(12)}(5,3;4,1)\hat{n}_{ks_k}(5,2)]\},\quad i\neq k.\end{aligned}\qquad(5.7)$$

We used in (5.7) that $U^{(12)}(1,2;3,4)=U^{(21)}(1,2;3,4)$ and also introduced the two-particle density matrix $\hat{\mathfrak{N}}_k$:

$$\hat{\mathfrak{N}}_k(1,2;\ 3,4)=\langle\hat{a}_{k1}{}^{+}\hat{a}_{k2}{}^{+}\hat{a}_{k3}\hat{a}_{k4}\rangle.\qquad(5.8)$$

In the perfect-gas approximation Eq. (5.6) is the usual Boltzmann equation in which the operator

$$-i\hat{Y}_{ks_k}/\hbar=\langle[\hat{a}_{k1}{}^{+}\hat{a}_{k2},\hat{U}_{int}]\rangle\qquad(5.9)$$

corresponds to the collision integral while the commutator of the matrices $\hat{T}^{(k)}$ and $\hat{n}_{kS_k}$ on the left-hand side of (5.6) describes the free motion of the particles between collisions. We need in what follows the explicit form of the virial corrections just in the commutator $[\hat{T}^{(k)},\hat{n}_{kS_k}]$, i.e., in the kinematic part of the kinetic equation. These corrections correspond to taking into account the liquid effects peculiar to a low density system and due to the effective self-consistent interaction of the gas molecules.

We are dealing with corrections connected with the functional virial expansion of the equilibrium distribution function (4.9), i.e., with the renormalization of the kinematic part arising when we linearize the kinetic equation with respect to small deviations from the actual equilibrium distribution function (4.9) and not from $n_{kS_k}^{(0)}$. The collision integral also vanishes when we substitute into it just the actual equilibrium density matrix. Both the collision integral, in the following denoted by $\hat{Y}'_{kS_k}$, and the kinematic virial corrections are determined by the interaction between the particles and enter into the matrix $\hat{Y}_{kS_k}$. A consistent rigorous derivation of the kinematic corrections at low temperatures $T\ll\hbar^2/mr_0^2$ was given in Ref. 6. Here we restrict ourselves in fact to an expansion of the kinetic equation in a functional series in powers of small perturbations of the density matrix, taking into account the above mentioned renormalization. The functional form of the expansion is determined by analogy with the low-temperature limit where it has a rigorous basis. The expansion coefficients are evaluated by means of the virial expression (4.9).

In the present paper we shall be interested merely in the spin degrees of freedom in a binary paramagnetic gas. In the matrices $\hat{T}^{(k)}$ and $\hat{n}_{kS_k}$ only those terms are therefore important for us which depend on the spin operators. For the energy of a single particle we have

$$\hat{T}^{(k)}=-\gamma_k\mathbf{S}_k\mathbf{H}.\qquad(5.10)$$

We linearize the kinetic Eq. (5.6). As in the preceding part of this paper we shall assume the external magnetic field to be weak so that in the linear approximation in **H** for the evaluation of the commutator $[\hat{T}^{k},\hat{n}_{kS_k}]$ we can neglect the contribution of the magnetic field to the polarization density matrix $\hat{n}_{kS_k}$. Taking what has been said into account we can always write the small non-equilibrium corrections to $\hat{n}_{kS_k}$ in the form

$$\delta\hat{n}_{kS_k}=\mathbf{S}_k\boldsymbol{\rho}_k(\mathbf{p})+\mathrm{Sp}_{s_m}\sum_{\mathbf{p}_2}C_{s_ks_m}(\mathbf{p},\mathbf{p}_2)\,n_{ks_k}^{(0)}(\mathbf{p})\,\mathbf{S}_m\boldsymbol{\rho}_m(\mathbf{p}_2),$$
$$m\neq k\qquad(5.11)$$

where $\boldsymbol{\rho}_k(\mathbf{p})\propto\exp(-i\omega t)$. Comparing (5.11) and (4.9) we check easily that

$$C_{s_ks_m}(\mathbf{p}_1,\mathbf{p}_2)=-\Phi_{s_ks_m}(\mathbf{p}_1,\mathbf{p}_2)/T,\qquad(5.12)$$

where the vector $\boldsymbol{\rho}_k$ differs from its value $\boldsymbol{\rho}_k^{(0)}$ in a perfect gas only by small virial corrections:

$$\mathbf{S}_k\rho_k=\mathbf{S}_k\rho_k^{(0)}\Big\{1+\mathrm{Sp}_{s_k'}\sum_{\mathbf{p}'}\Gamma^{(kk)}_{s_k s_k'}(\mathbf{p},\mathbf{p}')n^{(0)}_{ks_k}(\mathbf{p}')$$

$$-T^{-1}\,\mathrm{Sp}_{s_m}\sum_{\mathbf{p}_2}\Phi_{s_k s_m}(\mathbf{p},\mathbf{p}_2)n^{(0)}_{ms_m}(\mathbf{p}_2)\Big\}$$

$$+\mathrm{Sp}_{s_k'}\sum_{\mathbf{p}'}\Gamma^{(kk)}_{s_k s_k'}(\mathbf{p},\mathbf{p}')n^{(0)}_{ks_k}(\mathbf{p})\mathbf{S}_k'\rho_k^{(0)}(\mathbf{p}'). \qquad (5.13)$$

As before, to fix the ideas, we put $S_2=\frac{1}{2}$. Using (5.11), (5.12), (3.5) we can write Eq. (5.6) in the form

$$\frac{i\hbar}{\gamma_k}\mathbf{S}_k\frac{\partial\rho_k}{\partial t}=-[\mathbf{S}_k\mathbf{H},\mathbf{S}_k\rho_k]+\Big[\mathbf{S}_k\mathbf{H},\frac{S_k(S_m+1)(2S_m+1)}{3T}$$

$$\times\sum_{\mathbf{p}_2}\xi(\mathbf{p},\mathbf{p}_2)n_k^{(0)}(\mathbf{p})\mathbf{S}_k\rho_m(\mathbf{p}_2)\Big]+\hat{Y}'_{ks_k}(\rho_k,\rho_m),$$

$$k=1,2,\quad m\neq k. \qquad (5.14)$$

Acting on both sides of Eq. (5.14) with the spin operator S_k and after that averaging over the spins using the formula[13]

$$\mathrm{Sp}\{S_iS_kS_l\}=i\frac{S(S+1)(2S+1)}{6}\varepsilon_{ikl}, \qquad (5.15)$$

where ε_{ikl} is the antisymmetric unit tensor we find, after evaluating the commutators in (5.14) the required dynamic equations:

$$-\frac{\partial\rho_1}{\partial t}=\omega_{H1}[\mathfrak{M}\rho_1]-\omega_{H1}\frac{S_2(S_2+1)(2S_2+1)}{3T}$$

$$\times\Big[\mathfrak{M}\sum_{\mathbf{p}_2}\xi(\mathbf{p},\mathbf{p}_2)n_1^{(0)}(\mathbf{p})\rho_2(\mathbf{p}_2)\Big]$$

$$-\frac{1}{i\hbar}\mathrm{Sp}_{s_1}(S_1\hat{Y}'_{1s_1}),$$

$$(5.16)$$

$$-\frac{\partial\rho_2}{\partial t}=\omega_{H2}[\mathfrak{M}\rho_2]-\omega_{H2}\frac{S_1(S_1+1)(2S_1+1)}{3T}$$

$$\times\Big[\mathfrak{M}\sum_{\mathbf{p}_2}\xi(\mathbf{p},\mathbf{p}_2)n_2^{(0)}(\mathbf{p})\rho_1(\mathbf{p}_2)\Big]$$

$$-\frac{1}{i\hbar}\mathrm{Sp}_{s_2}(S_2\hat{Y}'_{2s_2}),$$

where we have introduced the notation $\omega_{Hk}=\gamma_k H$, $\mathfrak{M}=\mathbf{H}/H$. As in the exchange approximation the total spin of each of the components is conserved in the collision process all integrals containing $\mathbf{S}_k\hat{Y}'_{ks_k}$ and describing a change in the total spin in the collisions vanish when we integrate Eqs. (5.16) over momentum space. Integrating in (5.16) and changing to circular variables $\rho_k^{(+)}=\rho_{kx}+i\rho_{ky}$, $k=1,2$ we get finally

$$(\omega-\omega_{H1})\sum_{\mathbf{p}_1}\rho_1^{(+)}(\mathbf{p}_1)+\omega_{H1}\frac{S_2(S_2+1)(2S_2+1)}{3T}$$

$$\times\sum_{\mathbf{p}_1,\mathbf{p}_2}\xi(\mathbf{p}_1,\mathbf{p}_2)n_1^{(0)}(\mathbf{p}_1)\rho_2^{(+)}(\mathbf{p}_2)=0,$$

$$(5.17)$$

$$(\omega-\omega_{H2})\sum_{\mathbf{p}_1}\rho_2^{(+)}(\mathbf{p}_1)+\omega_{H2}\frac{S_1(S_1+1)(2S_1+1)}{3T}$$

$$\times\sum_{\mathbf{p}_1,\mathbf{p}_2}\xi(\mathbf{p}_1,\mathbf{p}_2)n_2^{(0)}(\mathbf{p}_2)\rho_1^{(+)}(\mathbf{p}_1)=0.$$

The terms in (5.1) containing $n_k^{(0)}$ are small virial corrections determining the shift in the magnetic resonance frequencies which one can easily evaluate by solving Eqs. (5.17) using perturbation theory.

The unperturbed solution is the precession of the two vectors $\mathbf{M}_1$ and $\mathbf{M}_2$ with frequencies ω_{H1} and ω_{H2} around the direction of the external magnetic field. The absolute magnitude of both vectors then remains unchanged. It therefore follows from the condition

$$M_{k0}\sin\varphi\approx M_{k0}m_k=\Big|\mathrm{Sp}_s\sum_{\mathbf{p}}\gamma_k\mathbf{S}_k\delta\hat{n}_{ks_k}\Big|, \qquad (5.18)$$

where φ is the angle of deviation of the vectors $\mathbf{M}_1$ and $\mathbf{M}_2$ from the direction of $\mathbf{H}$ that

$$\rho_k^{(+)}(\mathbf{p})=A\gamma_k n_k^{(0)}(\mathbf{p}),\quad A=\mathrm{const}. \qquad (5.19)$$

For convenience we assume that initially both vectors $\mathbf{M}_1$ and $\mathbf{M}_2$ were deflected by the same angle.

Substituting (5.19) into the set of Eqs. (5.17) we get for the resonance frequency shift

$$\frac{\omega_1-\omega_{H1}}{\omega_{H1}}=-\frac{S_2(S_2+1)(2S_2+1)(2S_1+1)}{3\gamma_1N_1T}$$

$$\times\sum_{\mathbf{p}_1,\mathbf{p}_2}\xi(\mathbf{p}_1,\mathbf{p}_2)n_1^{(0)}(\mathbf{p}_1)n_2^{(0)}(\mathbf{p}_2),$$

$$(5.20)$$

$$\frac{\omega_2-\omega_{H2}}{\omega_{H2}}=\frac{\omega_1-\omega_{H1}}{\omega_{H1}}\frac{S_1(S_1+1)}{S_2(S_2+1)}\frac{\gamma_1N_1}{\gamma_2N_2},$$

which is exactly the same as the phenomenological Eqs. (2.12) when we substitute Eqs. (3.1) and (3.8) for $\chi_{kk}^{(0)}$ and χ_{12}^{-1}.

We note that taking the kinematic liquid corrections into account in the kinetic equation for determining the spectrum of uniform oscillations of the magnetization is possible in principle for any temperature, whereas the consideration of similar terms for the evaluation of the dispersion law of high-frequency spin waves (spatially non-uniform fluctuations of the magnetic moment) in Boltzmann systems is admissible only at sufficienty low temperatures $T\ll\hbar^2/mr_0^2$, i.e., in the ultra-quantal region.[5,6] In all formulae one must then in the exact scattering amplitude retain only the main, s-wave term, while consideration of the other partial scattering amplitudes with higher angular momenta goes beyond the accuracy used. Such a limitation on the temperature range of applicability of the results obtained for non-uniform oscillations was connected with the necessity of comparing derivative terms in the kinematic part of the Boltzmann equation with the collision integral. However, in the case of spatially uniform magnetic moment distributions there are no such terms in the kinetic equation and the above mentioned limitation does not arise.

6. INTERACTION OF PARTICLES WITH UNITY SPIN: $S_1=S_2=1$.

From systematic considerations and also bearing in mind possible practical applications we evaluate the interaction function $\Phi_{S1,S2}(\mathbf{p}_1,\mathbf{p}_2)$ and the quantity χ_{12}^{-1} which determines the magnetic resonance frequency shift for a binary gas in which the particles of each kind have unity spin: $S_1 = S_2 = 1$. In that case the total spin S of two colliding particles can take on the values $S = 2$, 1,0, i.e., altogether $2S_1 + 1 = 3$ values. The corresponding values of the scattering amplitude will be denoted by f_2, f_1, f_0. To the extent that only the powers from 1 to $2S$ of the spin operator S are independent, while all higher powers can be expressed in terms of them,[14] the scalar interaction function for $S_1 = S_2 = 1$ can be written in the exchange approximation in the form

$$\Phi_{s_1s_2}(\mathbf{p}, \mathbf{p}') = B_0(\mathbf{p}, \mathbf{p}') + B_1(\mathbf{p}, \mathbf{p}')\mathbf{S}_1\mathbf{S}_2 + B_2(\mathbf{p}, \mathbf{p}')(\mathbf{S}_1\mathbf{S}_2)^2. \tag{6.1}$$

Using the formula for the eigenvalues of the operator for the scalar product of unit spins:

$$\mathbf{S}_1\mathbf{S}_2 = \frac{1}{2}\{S(S+1) - 4\} = \begin{cases} 1, & S=2 \\ -1, & S=1, \\ -2, & S=0 \end{cases} \tag{6.2}$$

reasoning as in the derivation of Eqs. (3.16), (3.17) we get from (6.1)

$$\begin{aligned} B_0(\mathbf{p}, \mathbf{p}') &= B_0(\mathbf{q}) = A_2/3 + A_1 - A_0/3, \\ B_1(\mathbf{p}, \mathbf{p}') &= B_1(\mathbf{q}) = (A_2 - A_1)/2, \\ B_2(\mathbf{p}, \mathbf{p}') &= B_2(\mathbf{q}) = A_2/6 - A_1/2 + A_0/3, \end{aligned} \tag{6.3}$$

where the functions A_l, $l = 0, 1, 2$ are expressed in terms of the scattering amplitudes f_l with different multiplicities using Eqs. (3.15) in which we must everywhere replace the index "$\pm$" by the index "l". Using now Eq. (3.2) in which we must substitute the interaction function (6.1) and the polarization density matrix (3.3) to evaluate the virial correction ΔF_{12} to the free energy, and then using Eqs. (3.6), (5.15) to find the trace over the spin variables, we find finally

$$\begin{aligned} \Delta F_{12} = {} & (2S_1+1)(2S_2+1) \\ & \times \sum_{\mathbf{p}_1,\mathbf{p}_2} \left\{ B_0(\mathbf{p}_1, \mathbf{p}_2) + \frac{S_1S_2(S_1+1)(S_2+1)}{3} B_2(\mathbf{p}_1, \mathbf{p}_2) \right\} \\ & \times n_1^{(0)}(\mathbf{p}_1) n_2^{(0)}(\mathbf{p}_2) + \frac{(2S_1+1)(2S_2+1)}{\gamma_1\gamma_2 N_1 N_2} \\ & \times \sum_{\mathbf{p}_1,\mathbf{p}_2} \left\{ B_1(\mathbf{p}_1, \mathbf{p}_2) - \frac{1}{4} B_2(\mathbf{p}_1, \mathbf{p}_2) \right\} \\ & \times n_1^{(0)}(\mathbf{p}_1) n_2^{(0)}(\mathbf{p}_2) \mathbf{M}_1\mathbf{M}_2, \end{aligned} \tag{6.4}$$

where $S_1 = S_2 = 1$. Integrating over the center-of-mass variables we find from (6.4)

$$\chi_{12}^{-1} = \frac{1}{\gamma_1\gamma_2} \frac{1}{(2\pi mT)^{3/2}} \int \left[B_1(\mathbf{q}) - \frac{1}{4} B_2(\mathbf{q}) \right] e^{-q^2/2mT} d^3q. \tag{6.5}$$

In the case when the colliding particles are identical (single-component gas) $f_2 = f_0 \equiv f_s$, i.e. also $A_2 = A_0 \equiv A_s$. Then $B_1 - B_2/4 = \frac{3}{8}(A_s - A_1)$, i.e., can be expressed in terms of the difference $A_s - A_1$ which is very natural for identical particles. We emphasize that at low temperatures identical particles with odd total spin do not interact with one another in the s-wave approximation $f_1 \approx 0$, $A_1 \approx 0$.

7. STRONG MAGNETIC FIELDS

When one lowers the temperature sufficiently there may arise a situation when the external magnetic field can no longer be considered to be weak in the sense that the criterion $\hbar\gamma_k H \ll T$, $k = 1,2$ is satisfied. It is therefore of interest to ascertain how the expressions obtained for the magnetic resonance frequencies change in the case of arbitrary magnetic field strengths. We consider the case of arbitrary fields using the example of a binary mixture of gases in which all particles have spin one-half: $S_1 = S_2 = \frac{1}{2}$.

In that case the polarization density matrix for each of the components is linear in the spin operator and can be written as follows:

$$n_{ks_k}^{(0)} = {}^1/_2 (n_k^{(+)} + n_k^{(-)}) + (n_k^{(+)} - n_k^{(-)}) \mathbf{S}_k \mathfrak{M}, \tag{7.1}$$

where $n_k^{(+)}$ and $n_k^{(-)}$ are the occupation numbers for particles with spins oriented, respectively, parallel and antiparallel to the direction of the external magnetic field. The quantities $n_k^{(\pm)}$ are normalized to the total number of particles (per unit volume) of a given spin orientation:

$$\sum_{\mathbf{p}} n_k^{(\pm)}(\mathbf{p}) = N_k^{(\pm)}, \quad N_k^{(+)} + N_k^{(-)} = N_k. \tag{7.2}$$

One verifies easily that in the Boltzmann temperature range where the gas molecules obey classical statistics Eq. (7.1) is equivalent to the expression

$$n_{ks_k}^{(0)} = n_k^{(0)} (1 + 2\alpha_k \mathbf{S}_k \mathfrak{M}), \quad \alpha_k N_k = N_k^{(+)} - N_k^{(-)}, \tag{7.3}$$

where α_k is the degree of polarization of the k th component, introduced in such a way that

$$\mathbf{M}_k = \gamma_k \alpha_k N_k \mathfrak{M}/2, \tag{7.4}$$

and $n_k^{(0)}$ is the Maxwell distribution function (3.4) of the unpolarized perfect gas.

As usual, we start with evaluating the contribution of the interaction to the free energy of the system. Substituting (7.3) into the virial expansion (3.2) we are led exactly to Eq. (3.7) for $S_1 = S_1 = \frac{1}{2}$. The free energy of the binary gas therefore contains as before only the scalar product of the magnetizations $\mathbf{M}_1 \cdot \mathbf{M}_2$ and is described by an expression similar to Eq. (2.1) for small $\mathbf{M}_1$ and $\mathbf{M}_2$:

$$F = f_{11}(M_1) + f_{22}(M_2) + \mathbf{M}_1\mathbf{M}_2/\chi_{12} - (\mathbf{M}_1 + \mathbf{M}_2)\mathbf{H} - H^2/8\pi, \tag{7.5}$$

where f_{11} anf f_{22} are independent of the direction of the vectors $\mathbf{M}_1$ and $\mathbf{M}_2$ while χ_{12}^{-1} is given by Eq. (3.8) for $S_1 = S_2 = \frac{1}{2}$. Substituting (7.5) into the dynamic Eqs. (2.2), (2.3) we check that we get for the resonance frequency spectrum the earlier Eq. (2.10) in which, however, the quantities M_{k0} are by no means connected to the external magnetic field through the relations $M_{k0} = \chi_{kk}^{(0)} H$ appropriate in the weak field case, but are expressed in terms of H through Eqs. (7.4). Finally we get

$$\omega_1 = \gamma H, \quad \omega_2 = \gamma H - \frac{\gamma^2 N}{2\chi_{12}} \operatorname{th} \frac{\gamma H}{2T}, \quad N = N_1 + N_2, \quad \gamma_1 = \gamma_2 \equiv \gamma. \tag{7.6}$$

At cryogenic temperatures $T \ll \hbar^2/mr_0^2$ the expression for the new resonance frequency (7.6) takes on the simple and physically obvious form

$$\omega_2 = \gamma H - \frac{\pi\hbar^2 a_2 N}{m} \operatorname{th} \frac{\gamma H}{2T}, \tag{7.7}$$

which agrees with the results of Ref. 6.

8. CONCLUSION

There is a rather large class of gases whose molecules possess paramagnetism even in their ground state. Among the inorganic substances are the well known O_2 (ground state term $^3\Sigma$), NO (ground state term $^2\Pi$), and the triatomic gases NO_2 and ClO_2 with total spin $S = \frac{1}{2}$. As a result of recent experimental achievements we can also regard spin-polarized atomic hydrogen H↑ as a long-lived practically stable paramagnetic gas.[3,4] There exists also a whole group of gaseous nuclear paramagnetics such as ^{3}He, HD, o-H_2 (orthohydrogen, and p-D_2 (paradeuterium). The formulae obtained earlier are, in principle, applicable to all these gases we mentioned. However, since quantum-mechanical corrections to the free energy of the gas decrease as the temperature rises, all effects will be most appreciable in those gases which condense at the possibly lowest temperatures and then have an appreciable saturated vapor pressure. Moreover, the rotational quantum $\Delta_{\rm rot}$ for the molecules of some of the above mentioned gases turns out to be appreciably smaller than the boiling temperature (even at the lowest pressures), so that the rotational degrees of freedom of the molecules will be strongly excited which leads to a strong coupling between the electron magnetic moment and the rotational moment of the molecule. This, in turn, greatly complicates the picture of paramagnetic resonance and makes it difficult to identify the phenomena considered in the present paper. For instance, $\Delta_{\rm rot}(O_2) = 2.1$ K and $\Delta_{\rm rot}(\mathrm{NO}) = 2.4$ K.

Thus, for a distinct observation of the predicted effects it is convenient to use various paramagnetic isotopes of hydrogen the molecules of which are characterized by large rotational quanta which appreciably exceed the boiling temperature: $\Delta_{\rm rot}(H_2) = 85.4$ K; $\Delta_{\rm rot}(D_2) = 43$ K; $\Delta_{\rm rot}(\mathrm{HD}) = 64$ K. However, since the mentioned hydrogen isotopes, and also ^{3}He, are nuclear paramagnetics and the range of the nuclear forces is appreciably shorter than the size of the molecules, in collisions of different molecules the nuclear wave functions overlap extremely little and the corresponding exchange interaction turns out to be vanishingly small. A completely different situation occurs if identical atoms are involved in the composition of the colliding molecules. In that case exchange of whole atoms rather than nuclei is possible in the reaction zone of the order of molecular dimensions. The exchange scattering amplitude will then be given by the size of the molecules as to order of magnitude, i.e., will be on an atomic rather than nuclear scale. Such a situation may, for instance, be realized in two-component mixtures of o-H_2 and HD (identical H atoms) or of p-D_2 and D_2 (identical D atoms). For these substances at $T \sim 10$ K the saturated vapor pressure corresponds to a density $N_k \sim 10^{18}$ to 10^{19} cm^{-3} so that estimates using Eq. (3.24) for $|a_2| \sim 1$ Å lead to the following shift of the paramagnetic resonance lines: $|\Delta\omega_k|/\omega_{Hk} \sim 10^{-5}$ to 10^{-4}.

Another interesting object in which possibly similar effects may manifest themselves is spin-polarized atomic hydrogen H↑ as after stabilization in a magnetic field due to hyperfine interaction the gas is a mixture of atoms in different spin states $|a\rangle = |\uparrow\downarrow\rangle - \varepsilon|\downarrow\uparrow\rangle$, $|b\rangle = |\uparrow\uparrow\rangle$, where ↑ and ↑ indicate the electron and nuclear spin z-components, and ε is a mixture parameter, i.e., H↑ can be considered to be a peculiar binary gas. In this case two kinds of magnetic dipole transitions are allowed: $|a\rangle \to |d\rangle$ and $|b\rangle \to |c\rangle$, where $|c\rangle = |\downarrow\uparrow\rangle + \varepsilon|\uparrow\downarrow\rangle$, $|d\rangle = |\downarrow\downarrow\rangle$. The resonance line corresponding to the transition $|b\rangle \to |c\rangle$ has been experimentally observed.[15] As different particles in a binary gas one can consider the same atoms in the ground state and in excited states which is realized in gaseous devices.

Quantitatively the effect of the resonance frequency shift is particularly large in the case when one of the components of a binary system is simply a gas of electrons the mass of which m_e is three orders of magnitude smaller than the atomic mass. In that situation the ultra-quantal case is practically always realized, $T \ll \hbar^2/mr_0^2$, and for a quantitative description one can use Eqs. (3.22) to (3.24) and (7.7) in the limit of low-energy scattering. For instance, in the case of weakly ionized gaseous Cs (one component is electrons and the other neutral atoms) at $T \sim 10^3$ K, $N_1 \sim N_2 \sim 10^{16}$ to 10^{17} cm^{-3}, $|a_2| \sim 10$ Å[16] we get for the additional resonance frequency ω_2: $|\omega_2 - \gamma H|/\gamma H \sim 10^{-5}$ to 10^{-4}. In semimagnetic semiconductors where the effect is caused by the scattering of electrons or holes by paramagnetic point defects (impurities) for typical values of the densities of the carriers $N_e \sim 10^{16}$ to 10^{17} cm^{-3} and of the defects $N_d \sim 10^{17}$ to 10^{18} cm^{-3} for $T \sim 10^2$ K, $|a_2| \sim 1$ Å, $m^* \sim 10^{-2}$ to 10^{-1} m_e (m^* is the effective carrier mass) the quantitative size of the effect $|\Delta\omega_k|/\omega_{Hk}$ turns out to be of the order of 10^{-3} to 10^{-1}.

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APPENDIX

To obtain all virial expansions we used quantum-mechanical rather than classical formulae. We formulate the criteria which allow us to establish how low the temperature must be in order that it is necessary for us to use just the quantum-mechanical approach. We perform all calculations using as an example a gas with particles which repel one another in accord with the law $U = \alpha/r^n$. When we consider the interaction between the gas particles classically we can evaluate the second virial coefficient using the formula[10]

$$B_{\rm class} = \frac{1}{2}\int (1 - e^{-U/T})\, dV = \frac{2\pi}{3}\left(\frac{\alpha}{T}\right)^{3/n} \Gamma\left(1 - \frac{3}{n}\right), \quad n > 3. \tag{A1}$$

The quantum-mechanical correction to the classical value (A1) is given by the expression[10]

$$B_{\rm quant} = \frac{\pi\hbar^2}{6mT^3} \int_0^\infty \left(\frac{dU}{dr}\right)^2 e^{-U/T} r^2\, dr = \frac{\pi\hbar^2 n}{6mT}\left(\frac{\alpha}{T}\right)^{1/n} \Gamma\left(2 - \frac{1}{n}\right). \tag{A2}$$

The ratio $B_{\rm quant}/B_{\rm class}$ thus turns out to be of the order of

$(\Lambda_T/r_T)^2$ where Λ_T is the thermal de Broglie wavelength from (3.25) and r_T some characteristic distance at which the potential energy of a particle is comparable to the average kinetic energy of its thermal motion:

$$U(r_T)=T. \tag{A3}$$

It is clear that in a dilute gas $r_T \ll N^{-1/3}$. In general, in a real gas $r_T^3 \lesssim T/P_c(T)$ where $P_c(T)$ describes the liquid-gas phase equilibrium curve in the diagram of state. At sufficiently low temperatures such that $\Lambda_T \sim r_T \ll N^{-1/3}$ it becomes necessary to use a quantum-mechanical discussion to describe effects connected with the interaction between the gas molecules.

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